

**ENHANCING POLYMER-POLYMER ADHESION VIA REACTIVE
COUPLING**

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ABSTRACT

We have studied promotion of interfacial adhesion for a model polystyrene (PS)/poly(methyl methacrylate) (PMMA) multilayer system through the coupling reaction of amine-terminal PS (PS-NH₂) and anhydride-terminal PMMA (PMMA-anh-pyr). The multilayer samples were made using a multilayer coextruder with a 20-layer feed block. The actual number of layers N was controlled by the number of multiplication dies n with the correlation $N = 20 \times 2^n$. The interfacial adhesion (G_c , critical fracture toughness) was measured with the asymmetric dual cantilever beam crack propagation test (ADCB test). The extent of the coupling reaction was quantified by measuring PMMA-anh-pyr conversion with a fluorescence detector coupled with the size exclusion chromatography (SEC). Interfacial morphology development was measured with atomic force microscope (AFM) and transmission electron microscope (TEM).

Slip occurs at the interfaces between immiscible polymer melts at high shear stress. We demonstrate that this reduces adhesion during coextrusion. When the shear stress experienced by an interface is low, interfacial slip is negligible and interfacial adhesion is high, comparable to a laminated interface. When the shear stress exceeds a critical value, interfacial slip begins and interfacial adhesion starts to decrease with shear stress. Above another critical stress, full slip has been developed at the interface and adhesion reaches a plateau value, which is about 1/3 of the equilibrium value. The changes in adhesion versus shear stress follow a master curve for different flow rates. This supports the hypothesis that polymer chains at the interface are disentangled by the shear stress during coextrusion. Annealing can restore adhesion on the reptation time scale, indicating that entanglements have been reestablished at the interface. The adhesion decrease during coextrusion can also be prevented by adding functional polymers to each layer and creating block copolymers *in situ* at the interface.

The interfacial morphology development induced by coupling reaction is also studied.

When Σ is low, the interface keeps flat or slightly roughened. When Σ is above the saturation coverage (Σ^*), the interface roughens significantly and interfacial emulsification starts. At this stage, micelles or swollen micelles are formed at the interface. However, this can only be observed for bilayers with high functional polymer concentration. When the concentration of functional polymer is low, the coupling reaction under annealing is slow and it takes a long time (over tens of hours) for copolymers to build up at the interface. Applying shear flows to such an interface can significantly accelerate the coupling reaction. We speculate shear flows expedite the mobility of functional groups and increase the possibility of complimentary functional groups to meet with each other at the interface. The coupling reaction has also been used to reactively compatibilize immiscible blends.